

Organochlorine and organophosphorous
compounds, total recoverable (0-3104-83)
and dissolved (0-1104-83), gas
chromatographic

	Code	
	Total recoverable	Dissolved
Aldrin -----	39330	39331
Chlordane -----	39350	39352
DDD -----	39360	39361
DDE -----	39365	39366
DDT -----	39370	39371
Diazinon -----	39570	39572
Dieldrin -----	39380	39381
Endosulfan -----	39388	82354
Eldrin -----	39390	39391
Ethion -----	39398	82346
Polychlorinated biphenyls ----	39516	39517
Polychlorinated naphthalenes -	39250	82360
Heptachlor -----	39410	39411
Heptachlor epoxide -----	39420	39421
Lindane -----	39340	39341
Malathion -----	39530	39532
Methoxychlor -----	39480	82350
Methyl parathion -----	39600	39602
Methyl trithion -----	39790	82344
Mirex -----	39755	39756
Parathion -----	39540	39542
Perthane -----	39034	82348
Toxaphene -----	39400	39401
Trithion -----	39786	82342

1. Application

This method is suitable for the determination of organochlorine insecticides, polychlorinated biphenyls (PCB's), polychlorinated naphthalenes (PCN's), and organophosphorous insecticides in water and water-suspended-sediment mixtures containing at least 0.01 µg/L of the analyte.

2. Summary of method

Organochlorine and organophosphorous compounds are extracted from water and water suspended-sediment mixtures with hexane. Organophosphorous compounds are determined on a gas chromatograph with flame-photometric detectors. The extracts are then purified using adsorption chromatography on an alumina column. If PCB's, PCN's, and toxaphene are present, the extracts are further purified using a silica gel column. The organochlorine compounds are then determined by gas chromatography using electron-capture detectors.

3. Interferences

Compounds having chemical and physical properties similar to the compound of interest may cause interference. Sulfur and organosulfur compounds will interfere, but these substances can be removed by treating the final extracts with mercury; however, the mercury treatment will also remove organophosphorous compounds.

4. Apparatus

4.1 *Alumina column*: Plug a disposable pipet with glass wool. Fill to a depth of 3 cm with alumina; then add 0.5 cm anhydrous sodium sulfate.

4.2 *Boiling chips*, micro, granules, Hengar H-1366C, or equivalent: Rinse with hexane, air dry, and heat overnight at 300 ° C.

4.3 *Concentrator, Kuderna-Danish (K-D)*, 250-mL flask, 5.0-mL receiver, and one-ball Snyder column.

4.4 *Evaporative concentrator*, Organomation N-Evap, or equivalent.

4.5 *Gas chromatograph*, Tracor 560, or equivalent.

4.5.1 The following conditions are recommended for organochlorine compounds:

Columns, borosilicate glass, 1.8 m x 2 mm id (inside diameter) operated at 200°C: Column packing materials are (1) 3 percent SP 2100 on 100/120 mesh Supelcoport, or equivalent; and (2) 1.5 percent SP 2250 + 1.95 percent SP 2401 on 100/120 mesh Supelcoport, or equivalent.

Detectors, electron capture, operated at 345°C.

Injection port temperature, 220 ° C.

Carrier gas, nitrogen or 5 percent methane in argon, flow rate 30 mL/min.

4.5.2 The following conditions are recommended for organophosphorous pesticides:

Columns, borosilicate glass, 1.8 m x 2 mm id operated at 175°C: Column packing materials are (1) 5 percent SP 2100 on 100/120 mesh Supelcoport, or equivalent; and (2) 2 percent SE-30 + 3 percent OV-210 on 100/120 mesh chromosorb HP, or equivalent.

Detectors, flame photometric, Melpar, or equivalent, operated at 210 ° C.

Injection port temperature, 210 ° C.

Carrier gas, helium or nitrogen, flow rate 30 mL/min.

4.6 *Glass filters*, 142 mm, 0.3 µm mean pore size, Gelman, or equivalent: Prepare the filters by rinsing with acetone and hexane, evaporating the solvent, and heating overnight at 300 ° C.

4.7 *Silica column*; to a 130 mm x 10 mm id glass tube having a coarse-porosity fritted disc, add 1 cm anhydrous sodium sulfate, 10 cm silica, and 1 cm anhydrous sodium sulfate.

5. Reagents

5.1 *Alumina adsorbent*, Woelm neutral aluminum oxide, or equivalent: Prepare deactivated adsorbent by adding 8 g deionized water to 92 g alumina and shake for at least 2 h on a wrist-action shaker. The alumina is tested for required deactivation by attempting to elute the organochlorine compounds of interest from a test column with 10 mL hexane. If the test compounds do not elute with 10 mL hexane, further deactivation is required.

5.2 *Mercury*, metallic, reagent grade.

5.3 *Pesticide mixed standards*, analytical reference grade, EPA analytical reference standards, or equivalent: Prepare individual stock solutions by weighing about 10 mg of each compound to at least three significant figures and quantitatively transfer each compound to a 25.0-mL volumetric flask. Dilute to volume with benzene and mix thoroughly. Aliquots are removed and diluted to volume with iso-octane to obtain the final concentrations listed in table 1.

5.4 *Silica adsorbent*, Woelm silica, 70-150 mesh, or equivalent: Prepare deactivated adsorbent by adding 0.2 g deionized water to 99.8 g silica and shake for at least 2 h on a wrist-action shaker. The deactivation is evaluated by attempting to reproduce the elution scheme in table 2. If the test compounds do not elute with 25 mL of hexane from the first silica fraction, additional deactivation is required.

5.5 *Sodium sulfate*, granular, anhydrous: Heat overnight at 300°C and store in a covered beaker at 130°C.

5.6 *Solvents*, benzene, hexane, and isooctane, pesticide residue quality, distilled in glass, Burdick and Jackson, or equivalent.

Table 1. Concentrations of pesticides in mixed standard solutions used for gas chromatograph calibration.

[Picograms per microliter]

Mixture number	Compound	High standard	Low standard
1 -----	Lindane	40	20
	Heptachlor	40	20
	Aldrin	40	20
	DDE	40	20
	DDD	40	20
	Mirex	40	20
	Methoxychlor	70	35
2 -----	Aldrin	40	20
	Heptachlor epoxide	40	20
	Dieldrin	40	20

	Endrin	40	20
3 -----	Chlordane	200	100
4 -----	Aldrin	40	20
	Endosulfan	40	20
	Perthane	40	20
	DDT	40	20
5 -----	Toxaphene	600	300
6 -----	p,p-DDE	40	20
	o,p-DDD	40	20
	o,p-DDT	40	20
7 -----	Aroclor 1016 (a PCB)	300	150
8 -----	Aroclor 1254 (a PCB)	400	200
9 -----	Aroclor 1260 (a PCB)	300	150
10 -----	Diazinon	100	60
	Malathion	130	65
	Dursban	100	50
	DEF	100	50
	Ethion	100	50
11 -----	Methyl parathion	100	50
	Ethyl parathion	100	50
	Methyl trithion	200	100
	Trithion	200	100

6. Procedure

All glassware must be washed in warm detergent solution, rinsed with organic-free water, and heated at 300°C overnight. Immediately before use, all glassware is rinsed with the solvent. Do not use stopcock grease on any ground-glass joints. For the determination of dissolved components, filter the sample through a glass fiber filter. Pour the filtrate into the original sample bottle and continue with the procedure.

6.1 A blank must accompany each group of samples. For each sample, rinse a 1,000-mL separatory funnel and a 125-mL Erlenmeyer flask with hexane.

6.2 Weigh the sample bottle plus the sample and record the weight to three significant figures.

6.3 Pour the sample into the separatory funnel and allow the bottle to drain completely. Weigh the empty bottle and cap, and record the weight to three significant figures. Calculate and record the sample weight.

Table 2. Column fractionation scheme for silica gel column for organochlorine insecticides, PCB's, and PCN's

Fraction 1 (20 mL hexane eluate)	Fraction 2 (30 mL benzene eluate)
Heptachlor 70 percent	Heptachlor 30 percent
DDE 85 percent	DDE 15 percent
Endosulfan	Lindane
Mirex	Perthane
PCB's	DDD
PCN's	DDT
	Methoxychlor
	Heptachlor epoxide
	Endrin
	Dieldrin
	Chlordane

6.4 Add 25 mL hexane to the sample bottle, rinse the sides thoroughly, and pour the solvent into the separatory funnel. The Teflon-lined cap is not rinsed because of the potential for contamination from solvent that has contacted the threads and surface beneath the Teflon liner. Shake the funnel vigorously for at least 1 min, venting often. Allow the layers to separate, and drain the

aqueous layer. Pour the hexane extract into the Erlenmeyer flask. Extract the sample twice more, using 25 mL hexane each time, and collect the extracts in the Erlenmeyer flask. Add about 0.5 g anhydrous sodium sulfate to the flask, cover with foil, and set aside for at least 2 h or refrigerate until analysis can continue.

6.5 Quantitatively transfer the extract with hexane to the K-D apparatus, add a boiling chip, and attach a Snyder column. Concentrate the extract to about 5 mL on a water bath maintained at about 90 ° C. Remove the K-D apparatus from the water bath, dry the joints with a towel, rinse the lower joint with hexane as the receiver is disconnected, and place the receiver on an evaporative concentrator to reduce the volume to about 0.5 mL. Rinse the walls of the receiver two or three times with a few drops of hexane during the final concentration. Dilute the extract to 1.0 mL and analyze the extract by gas chromatography using flame-photometric detectors for the determination of organophosphorous insecticides.

6.6 Prepare gas chromatograph calibration curves daily with the mixed standards (table 1). Operating conditions must be identical to those used for sample analysis. Calibrate both analytical columns. Record the volume of the standard injected and the retention time and integrated peak area of each component in the standard.

6.7 Inject an aliquot of sample extract into the gas chromatograph. Record the volume injected. Identify peaks by retention time. The identification must be made on both analytical columns. Record the retention time and integrated area of any identified peak. Dilute any extract containing an identifiable component above the highest standard (see table 1) to bring it within that range. Identified compounds may be quantitated using the calculations described below.

6.8 Following analysis for organophosphorous insecticides, transfer the extract to an alumina column. Elute with hexane and collect 10 mL. Add 1.0 mL iso-octane to the eluate and reduce the volume to 1.0 mL on an evaporative concentrator, rinsing the sides of the receiver two or three times with iso-octane during the concentration. Analyze the concentrated eluate by gas chromatography as described in steps 6.6 and 6.7 using electron-capture detectors for organochlorine compounds.

6.9 If the extract contains multiple component mixtures such as PCB's, PCN's, toxaphene, or interferences, it might be necessary to perform the silica gel cleanup to obtain the fractionation shown in table 2.

7. Calculations

7.1 Calculate the response factor of each identified component in the calibration standard using the equation

$$RF = \frac{A_1}{C_S \times V_1}$$

where

RF = response factor of identified component in calibration standard, in area/pg,

C_S = concentration of standard, in pg/ μ L,

V_1 = volume of standard injected, in μ L, and

A_1 = integrated peak area of identified component in calibration standard.

7.2 Calculate the concentration of each identified component in the original water sample from the equation

$$\text{Concentration } (\mu\text{g/L}) = \frac{A_2 \times V_2}{V_3 \times W \times RF}$$

where

RF = response factor of identified calibration standard component, in area/pg,

A_2 = integrated peak area of identified sample component,

V_2 = final volume of sample extract, in mL,

V_3 = volume of sample extract injected, in μ L, and

W = weight of sample in g, expressed in mL (1.000 mL = 1.000 g)

8. Report

8.1 Report concentrations of organochlorine compounds (except chlordane, perthane, toxaphene, PCB's, and PCN's) and organophosphorous insecticides as follows: less than 0.01 μ g/L, as "less than 0.01 μ g/L"; 0.01 to 0.10 μ g/L, one significant figure; 0.10 μ g/L and above, two significant figures.

8.2 Report concentrations of chlordane, perthane, PCB's, and PCN's as follows: less than 0.1 µg/L, as "less than 0.1 µg/L"; 0.1 µg/L and above, two significant figures.

8.3 Report concentrations of toxaphene as follows: less than 1.0 µg/L, as "less than 1.0 µg/L"; 1.0 µg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved insecticides and PCB's (Arochlors 1248 and 1254) in distilled water for seven replicates at each concentration are as follows:

<i>Compound</i>	Concentration spiked (µg/L)	Mean concentration determined (µg/L)	Relative standard deviation (percent)
Chlordane -----	0.13	0.09	13
	0.25	0.15	30
	0.50	0.39	13
Arochlor 1248 -----	0.20	0.20	13
	0.41	0.28	23
	0.82	0.55	8.8
Arochlor 1254 -----	0.12	0.07	28
	0.24	0.20	15
	0.49	0.24	4.1
Lindane -----	0.014	0.012	12
	0.027	0.035	11
	0.054	0.064	7.3
Heptachlor -----	0.010	0.007	15
	0.020	0.015	16
	0.040	0.042	4.3
Aldrin -----	0.009	0.008	17
	0.017	0.016	14
	0.035	0.042	5.0
Perthane -----	0.12	0.038	9.4
	0.23	0.17	16
	0.47	0.14	4.0
Endosulfan-----	0.021	0.015	8.9
	0.042	0.047	5.2
	0.084	0.077	6.7

<i>Compound</i>	<i>Concentration Spiked (µg/L)</i>	<i>Mean concentration determined (µg/L)</i>	<i>Relative standard deviation (percent)</i>
p,p-DDE -----	0.020	0.025	19
	0.040	0.051	11
	0.080	0.15	3.3
p,p-DDD -----	0.030	0.020	13
	0.060	0.062	9.5
	0.12	0.13	6.2
p,p-DDT -----	0.053	0.033	19
	0.11	0.10	7.7
	0.21	0.23	7.0
Methoxychlor -----	0.022	0.016	8.5
	0.044	0.041	7.9
	0.087	0.079	5.0
Mirex-----	0.020	0.012	34
	0.041	0.028	21
	0.082	0.072	4.9
Diazinon -----	0.23	0.15	20
Malathion -----	0.26	0.18	32
Methyl parathion ---	0.22	0.16	9.2
Parathion-----	0.15	0.12	6.3
Methyl trithion-----	0.15	0.07	12
Ethion -----	0.15	0.12	7.4
Trithion -----	0.25	0.18	7.6

9.2 It is estimated that the percent relative standard deviation for total recoverable insecticides and PCB's will be greater than that reported for dissolved insecticides and PCB's.

Selected references

- Goerlitz, D.F., and Brown, Eugene, 1972, Methods for analysis of organic substances in water: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A3, 40 p.
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- _____, 1972, Chlorinated naphthalenes in pesticide analysis: Bulletin of Environmental Contamination and Toxicology, v. 7, p. 243-251.
- _____, 1974, Determination of chlorinated insecticides in suspended sediment and bottom material: Journal of the Association of Official Analytical Chemists, v. 57, p. 176-181.